

*Studies of the Processes Operative in Solutions. XXIII.—The
Hydrolysis of Methylic Acetate by Acids.*

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A.—Introduction.

One of the main objects in view throughout this series of studies of the processes operative in solutions has been to discover the nature of the changes which attend dissolution, particularly the extent to which substances undergo hydration when dissolved in water; another primary object has been to unravel the nature of the process of hydrolysis. The evidence thus far obtained has been always such as to show that the phenomena are far more complex than is usually supposed and even to discredit the interpretation that it is now customary to give of them.

In Communication XII of the series, I have given an account of experiments made with improved apparatus and with extreme care of the behaviour of cane sugar towards chlorhydric and nitric acids and of the influence of certain chlorides and nitrates on the rate of change. It was shown that the rate of hydrolysis could not be accurately expressed by any simple formula, as it was not even proportional to the concentration of the sugar, though it was approximately so when the molecular ratio of sugar to water was not high. Evidence was adduced to show that water as such, *i.e.* free water, did not play any part in the change but acted solely as solvent and that the active factor of the interaction besides the sugar was the hydrated acid catalyst.

A novel method was devised whereby the apparent molecular hydration of the acid was arrived at.

[It was assumed that a certain number n of molecules of water (H_2O) was combined with or controlled by one molecule of acid and that only the remaining, "free" water acted as diluent. The values of K , expressing the velocities of hydrolysis when one molecular proportion of acid was used in the presence of different numbers of molecular proportions of water, were multiplied by the total number minus n of molecular proportions of water, n being given a series of trial values. The products were plotted against the total water, a curve being obtained for each value of n (see Diagram 3 and Diagram 1, Part XXIII). It will be seen from the diagrams that each curve rises to a maximum and then falls as the dilution is increased, the maxima

occurring at points corresponding to greater and greater dilution as the value of n is increased. If the degree of hydration increase with dilution, it is obvious that, until maximum hydration is reached, a particular value of n can express the true degree of hydration only at one concentration, which has been taken to be that corresponding to the maximum on the curve when it is horizontal; in other words, when the rate of change of the value of the product is momentarily nil. The value of the product at each of the maxima is taken as the molecular hydrolytic activity of the acid at the corresponding dilutions. With increasing dilution the molecular hydrolytic activity decreases towards a minimum, while the values of n increase towards a maximum.

The values of n so obtained have been intentionally called *apparent* hydration values, as it must be recognised that, although they may possibly in the main represent actual hydration, they are probably dependent to a considerable extent on the balancing of opposed effects and also on the method of expressing dilution.—*November 28, 1912.*]

Though it is probably far more rational to express dilution in terms of the molecular proportions of solvent (here free water) than to adopt the old volume method still favoured by many chemists, yet, in the case of concentrated solutions, there is no method which is not open to objection.

A similar series of experiments with raffinose—a sugar closely allied to cane sugar but of higher molecular weight—was described by Dr. Glover in Communication XIV of the series. Very similar values, representing the apparent degree of hydration of hydrogen chloride and chlorides of the alkali metals, were obtained by means of both sugars, though, on using raffinose as hydrolyte, the values deduced for nitric acid and nitrates were slightly lower than those obtained by means of cane sugar.

By using methylic acetate as hydrolyte in place of cane sugar, Armstrong and Watson (in Part VII) deduced apparent hydration values for a number of salts which were much lower than those found by means of cane sugar. The subject was further discussed in Communication VIII and the conclusion formulated that “hydration values” should vary from case to case and that the highest values should be obtained by using hydrolytes and hydrolysts which form relatively stable hydrols in solution (VIII, p. 109). Methylic acetate was spoken of in this communication as a “weak hydrolyte.”

One object in carrying out the series of experiments reported in the present communication was to verify the correctness of Armstrong and Watson's conclusions.

Another important object was to confirm the validity of the method described above of finding the apparent molecular hydration of the acid. As the two hydrolytes, cane sugar and raffinose, were so similar in

character and the method of following the course of change the same, it appeared to be essential to apply the method to the case of the hydrolysis of substances of entirely different character, such as would render it possible to evaluate the course of change by a purely chemical method. It was expected that if the conclusion provisionally formulated by Armstrong and Watson were confirmed, namely, that the apparent hydration values of salts were lower when methylic acetate was used than when cane sugar was the hydrolyte, there would be a corresponding difference in the apparent hydration values of the acid.

B.—*Experimental.*

The ordinary materials used were purified in the manner described in previous communications. Methylic acetate was obtained at first from Kahlbaum but as the purchased material contained a considerable amount of impurity from which it could not be separated in a satisfactory manner by fractional distillation, I prepared the ethereal salt myself in accordance with the directions given by Wade,* substituting methylic for ethylic alcohol.

The product had the boiling point and density characteristic of methylic acetate and also gave satisfactory results on analysis, yielding 1.002 molecular proportions of acetic acid when hydrolysed by a slight excess of baryta solution.

In making the experiments, the requisite amounts of water and chlorhydric acid were weighed out into a conical 200 c.c. Jena flask; instead of weighing out the exact amount required, it was found to be more convenient to add approximately the desired proportion of methylic acetate and then at once close the flask with a caoutchouc stopper and again weigh in order to ascertain the amount of acetate added; correction was always made for the air displaced.

In the experiments in which hydrolysis took place so rapidly that it was necessary to carry out the titration as soon as possible after mixing the substances, the methylic acetate was weighed into a short wide test-tube suspended in the flask and the solution was heated to the required temperature in the thermostat before admixture was effected; in other cases the substances were well mixed before placing the flask in the thermostat. The experiments were carried out at $25^{\circ} \pm 0.01^{\circ}$.

Titration was made at intervals of 10 or 15 minutes or at longer intervals in the case of the more dilute solutions. A dilute solution of baryta was used as alkali. The rather large error by which such determinations are usually affected was reduced to a minimum in the following manner:—

* 'Chem. Soc. Trans.,' 1905, p. 1656.

The rubber stopper used to close the flask was provided with a hole just large enough to admit the stem of the pipette and this was closed with a small glass stopper; there was, therefore, but little chance of vapour escaping into the air on removing the subsidiary stopper when taking out the sample of liquid from the flask. The pipette was warmed to 25° in a tube in the thermostat before it was introduced. In taking samples, the desired approximate quantity of the solution was sucked up into the pipette and at once run into an excess of carefully neutralised solution of sodic acetate and the weight determined. In this way, the time required to remove the sample and run it into the acetate solution (which was used in order to prevent further hydrolysis of the sample) was reduced to a few seconds and the error of a pipette measurement was avoided. The titrations were effected by using a very slight excess of baryta solution and estimating the excess by an N/50 solution of hydrogen chloride. The strength of the baryta solution was determined for each experiment and for the end points by means of a weighed quantity of the standard chlorhydric acid used in the experiments; this precaution is rendered very necessary on account of the change of density from day to day in the baryta solution as the temperature varies.

In all the experiments water and methylic acetate were used in the proportion of 120 molecules of the former to 1 of the latter, together with from 0.6 to 4 molecules of hydrogen chloride.

C.—*Deduction of Velocity Coefficient.*

The velocity coefficient, K , of the interaction under the different conditions was deduced from the equation

$$\frac{dx}{dt} = K(a-x) - K'x^2,$$

in which a is the original molecular concentration of the methylic acetate and x the amount hydrolysed at time t . To avoid using the unwieldy equation obtained on integrating this expression, the rate of change dx/dt was estimated directly by plotting the percentage change against the time and determining the tangent to the curve at every 5 per cent. change by means of a black silk thread—a method which has many advantages. The value of K' in terms of K was deduced from the quantities of the interacting substances present at equilibrium, when $dx/dt = 0$, and consequently

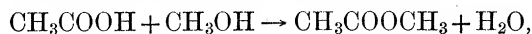
$$K' = \frac{K(a-x_{\infty})}{(x_{\infty})^2},$$

when x_{∞} is the amount hydrolysed at equilibrium.

The graphic method of obtaining velocity coefficients is very much simpler

and in every way more satisfactory than that of using the complicated mathematical formula in cases in which the experimental error is larger than that involved in estimating the value of the tangent.

It has been usual to assume that in dilute aqueous solution methylic acetate is almost completely hydrolysed and that under such conditions the small amount of change in a reverse direction, viz. :



is negligible.

As the water remains practically unchanged in amount, the interaction in such a case may be treated as a case of simple unimolecular change in which, finally, the methylic acetate is almost completely hydrolysed.

My experiments show, however, that even at the low concentrations used a considerable proportion of the methylic acetate remains unhydrolysed when equilibrium is attained, the degree of hydrolysis in no experiment exceeding 95 per cent. It consequently seems imperative to take into account the reverse change of etherification in deducing the velocity coefficients. It should be pointed out that if this reverse change be neglected, the magnitude of the velocity coefficient obtained is considerably altered, though its constancy may be affected but slightly; whence it follows that the fact that a constant value is obtained for K on the assumption that the interchange is complete and proceeds as a unimolecular change is no proof that this assumption is correct. To illustrate these points, values for the velocity coefficient in the case of an experiment when the degree of hydrolysis at equilibrium was 93.73 per cent. have been deduced, both taking into account the reverse change and omitting it. In Table I, under K_1 are given the values (multiplied by 10^5) obtained on taking into account the two opposing interactions. Under K_2 are given the values arrived at by neglecting the reverse change and assuming that at equilibrium the whole of the methylic acetate has been hydrolysed. This is the procedure that has been generally followed by previous observers. In the particular experiment, as 6.27 per cent. of acetate remained unhydrolysed, the values taken as the concentration of the acetate are lower to this extent than the true values throughout the experiment. Nevertheless, it will be observed that the values under K_2 are almost as constant as the true values under K_1 , though of considerably greater magnitude.

Under K_3 are given the values obtained on neglecting the reverse action and considering the actual amounts of methylic acetate present, assuming also that the action is ultimately complete—a course sometimes adopted. The values are fairly constant at first but fall off as the interaction proceeds.

It is very much easier to consider only the acetate that can be hydrolysed

than to estimate the total amount present; for this reason the method by which the values under K_2 are deduced has been generally adopted previously. In the present series of experiments, however, as the solutions were made up by weight and practically pure methylic acetate was used and as weighed quantities were taken for titration, it has been possible to estimate the total amount of acetate left unhydrolysed after different intervals of time in each experiment.

Table I.

Percentage change.	$\frac{dx}{dt} \times 10^5$	K_1	K_2	K_3
20	758	951	1028	948
25	710	952	1033	947
30	664	957	1042	949
35	612	954	1042	941
40	556	945	1035	927
45	503	939	1032	915
50	449	931	1027	898
55	402	938	1038	893
60	356	951	1055	890
65	304	950	1058	869

It is, perhaps, well to call attention to these examples as an illustration of the difficulties attending the reduction of observations such as those under discussion.

The data from a typical experiment are given in Table II.

Table II.—Typical Experiment. 120 Molecular Proportions of H_2O , 1 of CH_3COOCH_3 , and 1.5 of HCl .

Time in minutes.	A.	B.	C. Percentage change.	D. Percentage change.	$\frac{dx}{dt} \times 10^5$	$K \times 10^5$
0	5.303	0.359	10.84			
20	5.549	0.605	18.27	15	373	440
40	5.78	0.836	25.25	20	351	440
60	5.989	1.045	31.55	25	331	444
80	6.18	1.236	37.33	30	308	444
100	6.355	1.411	42.62	35	285	444
120	6.51	1.566	47.28	40	260	441
140	—	—	—	45	238	443
160	6.789	1.845	55.71	50	215	444
180	—	—	—	55	192	445
200	—	—	—	60	167	442
220	7.096	2.152	64.98			
240	—	—	—			
260	—	—	—			
280	7.352	2.408	72.71			
Final	8.073	3.129	94.47			
(Complete hydrolysis calc.)	8.256	3.312	100.0			
				Mean		443

Column A gives the baryta solution equivalent to 1 gram. of solution (found by titrating from 5 to 10 gram.).

Column B gives the baryta solution equivalent to the acetic acid in 1 gram. of solution. The values are obtained by deducting 4.944, the amount of baryta solution equivalent to the HCl in 1 gram. of solution, from the numbers in Column A.

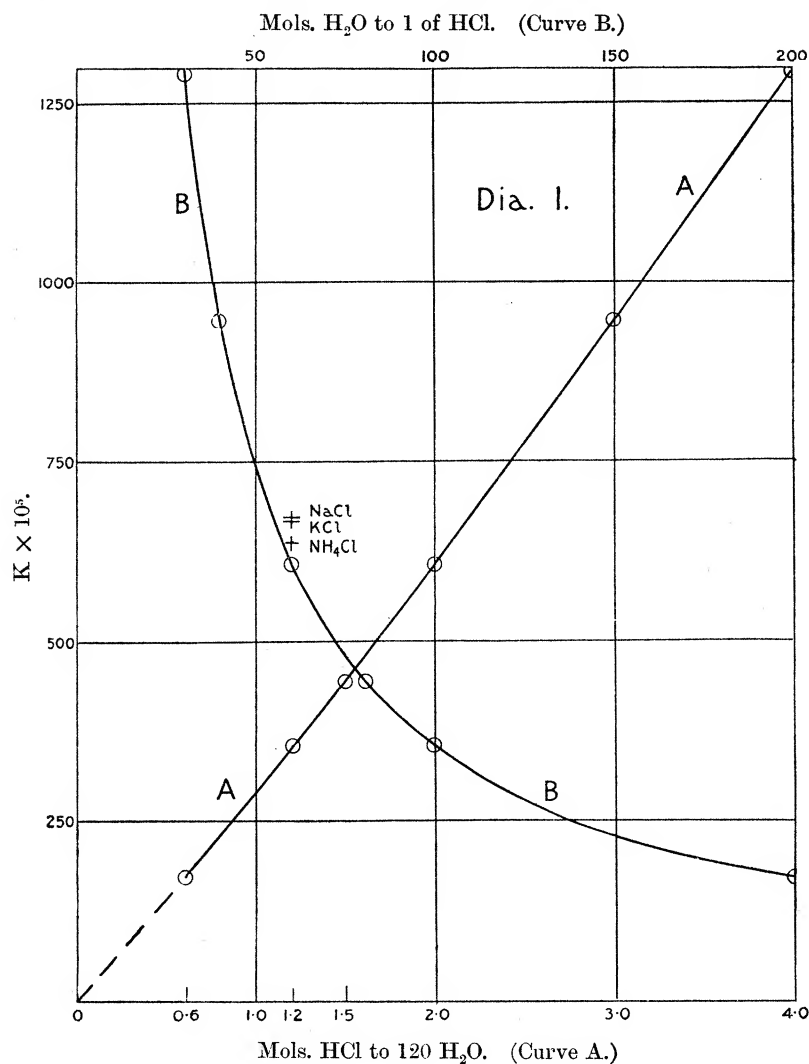
Column C gives the calculated percentage of the methylic acetate hydrolysed.

Column D gives the percentage hydrolysis corresponding to the rates of change in the following column determined from the curve.

Table III contains the velocity coefficients (multiplied by 10^5) deduced from the different experiments. In Diagram 1 is shown graphically the relation of the velocity coefficients to the concentration of the chlorhydric acid, Curve A being that obtained when the concentration is expressed as the molecular proportion of hydrogen chloride to 120 of water, Curve B when the dilution is expressed in terms of the number of molecular proportions of water (H_2O) to 1 of hydrogen chloride.

Table III.—Values of $K \times 10^5$, from Experiments with 120 Molecular Proportions of H_2O , 1 of CH_3COOCH_3 , and from 0.6 to 4.0 of HCl.

Percentage change.	Molecular proportions of hydrogen chloride.					
	0.6	1.2	1.5	2.0	3.0	4.0
10	171	354				
15	170	349	440			
20	170	349	440	604	951	1282
25	170	349	444	597	952	1271
30	170	357	444	589	957	1282
35	171	356	444	595	954	1292
40	171	352	441	598	945	1310
45	171	357	443	610	939	1309
50		355	444	605	931	1295
55		357	445	610	938	1301
60		357	442	620	951	1319
65				608	950	1295
70				630		1269
75						1287
Mean	170.5	354	443	606	947	1293



D.—*Change in the Degree of Hydrolysis with Variations in the Concentration of the Acid Catalyst.*

The end values obtained in the experiments described are such as to show that the percentage of methylic acetate hydrolysed at the time of equilibrium is not independent of the concentration of the hydrogen chloride used as catalyst. To make sure that there was a real displacement of the point of equilibrium and that the apparent lowering of the degree of hydrolysis by the presence of the hydrogen chloride was not due to the formation and escape of methylic chloride, several experiments were made in which the

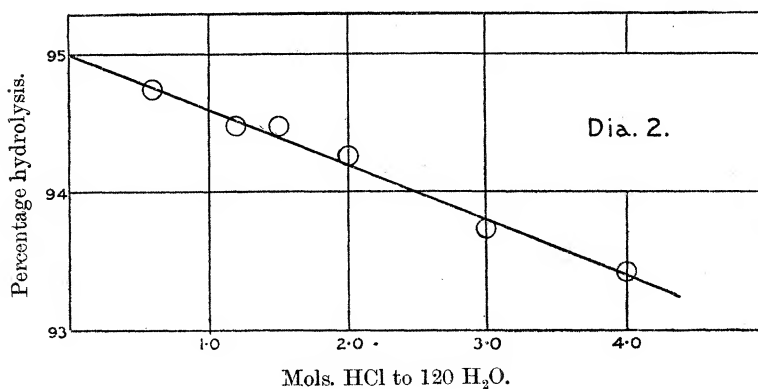
point of equilibrium was approached from the other end, beginning with methylic alcohol, acetic acid, water and different amounts of hydrogen chloride. The points of equilibrium were practically the same as those obtained by hydrolysis, showing that there was an actual displacement of the point of equilibrium and an apparent change in the ratio of K' to K as the concentration of the acid catalyst was increased. This point will be discussed in a later section.

In Table IV is given in Column A the percentage of methylic acetate hydrolysed in the presence of the different amounts of hydrogen chloride indicated in the first column, whilst in Column B is given the percentage of acetic acid and methylic alcohol left uncombined in the etherification experiments.

In Diagram 2 is shown graphically the degree of hydrolysis attained in the presence of different amounts of hydrogen chloride.

Table IV.—Change in the Percentage of Methylic Acetate Hydrolysed at Equilibrium caused by Change in the Concentration of Hydrogen Chloride.

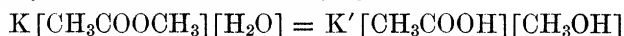
Molecular proportions of HCl.	A. (Hydrolysis.)	B. (Esterification.)
0·6	94·74	
1·0	—	94·63
1·2	94·48	
1·5	94·47	
2·0	94·27	94·4
3·0	93·73	93·94
4·0	93·42	



E.—*Limitations of the Deductions that may be made from the Results arrived at by the treatment of the Experimental Data according to the Principle of Mass Action.*

It is now necessary to consider the adequacy of the methods used heretofore in discussing the results of experiments such as have been described. The view has been too generally held perhaps that the catalyst is not a necessary component of the system within which the change occurs but only accelerates its rate; and it has been wrongly assumed that the position of equilibrium is not changed by the presence of the catalyst or by alteration of its concentration. It has further been universally held that water as such enters into the interaction, no distinction having been made between the water which plays an active part in the change in conjunction with the catalyst* and the water which acts only as solvent or diluent.

The mass action equations expressing the relation between the rates of hydrolysis and esterification and the concentrations of the interacting substances and that for the conditions at equilibrium have too frequently been based on the conventional chemical equations which express only the initial and final states without reference to the course of the change and the part played by the catalyst. Thus in the case of hydrolysis it has been generally assumed that because one molecule of water (hydrone) is used up for every molecule of hydrolyte hydrolysed, the rate of hydrolysis is therefore proportional to the product of the concentrations of the hydrolyte and the water. Again, in the case of the equilibrium between methylic acetate, water, acetic acid and methylic alcohol, the following equation



has always been considered to express the facts accurately, the bracketed quantities being the molecular concentrations (strictly speaking, the active masses) of the substances in equilibrium. The constancy in the ratio of K' to K that has been believed to persist when the relative proportions of the various substances have been altered has appeared to confirm the assumption that the active masses of the interacting substances are correctly expressed by the above equation.

The fact has apparently been overlooked, however, that even though the ratio of K' to K remain constant, it does not follow that the factor $[\text{H}_2\text{O}]$ of the mass action equation necessarily represents one of the substances entering directly into the interaction. It may be a factor representing merely the degree of dilution.

* For the purposes of this discussion the anhydrous acid is represented as the catalyst. In actual fact, the active agent is probably some form of hydrated compound derived from the anhydrous acid and water.

Confusion has probably arisen through the substitution of relative molecular proportions of the interacting substances for their concentrations in the above equation. When the four substances are dissolved in a given quantity of some solvent such as acetone or when one of the interacting substances is in large excess and may be regarded as constant, the concentration of the different substances is not lost sight of; when, however, there is no outside solvent and none of the four substances is in large excess, it is much easier to consider their relative molecular proportions. Provided that the equation express the interaction accurately and that the active mass of each substance be proportional to its total quantity, relative molecular proportions may be justly substituted for concentrations. This follows from the symmetrical nature of the equation. Whether we express the concentration as the number of molecular proportions either (*a*) in a given volume or (*b*) compared with that of one of the interacting substances or (*c*) compared with the total number of molecular proportions present, this dilution factor is the same for both sides of the equation and so does not affect it.

If, however, the water function mainly as diluent and be not strictly a factor in the interaction, the equation becomes unsymmetrical and a dilution factor must be introduced. In Part XII the view was put forward that in the case of the hydrolysis of cane sugar the interaction was between the sugar and the hydrated catalyst, the water uncombined with the catalyst functioning merely as solvent. It is highly probable that this is the case also in the hydrolysis of ethereal salts. If the action of the catalyst be considered, it is well known that the velocity coefficient for the rate of hydrolysis is nearly proportional to the concentration of the catalyst when the latter varies in concentration. This is very clearly shown by the approximate straightness of Curve A in Diagram 1, which shows the relation of the velocity coefficient *K* to the concentration of the hydrogen chloride. It shows, further, from the part extrapolated to zero concentration of acid, that in the absence of catalyst the rate of hydrolysis is reduced to zero. In other words, water alone has probably no power of effecting the hydrolysis of methylic acetate. This argument does not, of course, preclude the view that has been frequently adopted, that the action is between the water and a compound of the acetate with the catalyst. It appears far more likely, however, that the interaction is between the ethereal salt and a compound of the catalyst with water, *i.e.* with the hydrated catalyst. The mechanism of hydrolysis will be fully discussed at a later stage; but, for the present, let us assume that hydrolysis is effected by the interaction of the ethereal salt and hydrated catalyst and that the water uncombined with the catalyst functions merely as solvent and diluent. If the proportion of the solvent (*i.e.* the free water) be large

it makes little difference whether we reckon concentration as the number of molecular proportions either in a given volume or compared with a given number of molecular proportions of the solvent. The concentrations of the interacting substances may be expressed consequently as the ratio of their molecular proportions to those of the diluent water. The equation expressing the conditions at equilibrium thus becomes

$$K \frac{[\text{CH}_3\text{COOCH}_3]}{[\text{H}_2\text{O}]} \times \frac{[\text{hydrated catalyst}]}{[\text{H}_2\text{O}]} = K' \frac{[\text{CH}_3\text{COOH}]}{[\text{H}_2\text{O}]} \times \frac{[\text{CH}_3\text{OH}]}{[\text{H}_2\text{O}]} \times \frac{[\text{hydrated catalyst}]}{[\text{H}_2\text{O}]},$$

when the bracketed quantities are the relative molecular proportions of the various substances.

On simplification this becomes

$$K [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}] = K' [\text{CH}_3\text{COOH}][\text{CH}_3\text{OH}],$$

in which the factor $[\text{H}_2\text{O}]$ is merely a dilution factor and does not stand for one of the interacting substances. Any other expression for the dilution can be substituted equally well. The above simplified equation is thus very liable to be misinterpreted and wrong deductions have frequently been made from the results obtained by its use.

If the water be not in large excess, it is obvious that it is not legitimate to use it as a dilution factor and the equation is valid only on the highly improbable assumption that the four factors represent the interacting substances and that the active part of each is proportional to its concentration even when the degree of concentration is high.

Since the completion of this investigation, Jones and Lapworth* have published the results of an investigation of the action of hydrogen chloride on the equilibrium between ethylic acetate, water, ethylic alcohol and acetic acid. In all their experiments the proportion of water was small and could not possibly be regarded as a measure of the dilution. They considered merely relative molecular proportions and found that the value of ψ , where

$$\psi = \frac{[\text{H}_2\text{O}(\text{total})][\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]},$$

rose from 4 to 8 at least when the concentration of the hydrogen chloride used as catalyst varied over wide limits. They assumed that this variation in the value of ψ was due to some of the water forming a hydrate of the hydrogen chloride and calculated that approximately two molecules of water were associated with each molecule of hydrogen chloride present, though the existence of higher hydrates in a partly dissociated condition was

* 'Chem. Soc. Journ.,' 1911, p. 1427.

not excluded. Apart from the improbability of the degree of hydration remaining the same and so low over large ranges of concentration, it is obvious that their conclusions can be in no way valid except on the assumption that water as such is one of the interacting substances; that the active masses of each of the four substances are proportional even in strong solutions to their concentrations; also that the active mass of the water is proportional to that part of it unassociated with the hydrogen chloride, *i.e.* proportional to the pure water present which has no power to effect the hydrolysis of pure ethylic acetate. It is obvious that little weight can be attached to their conclusions.

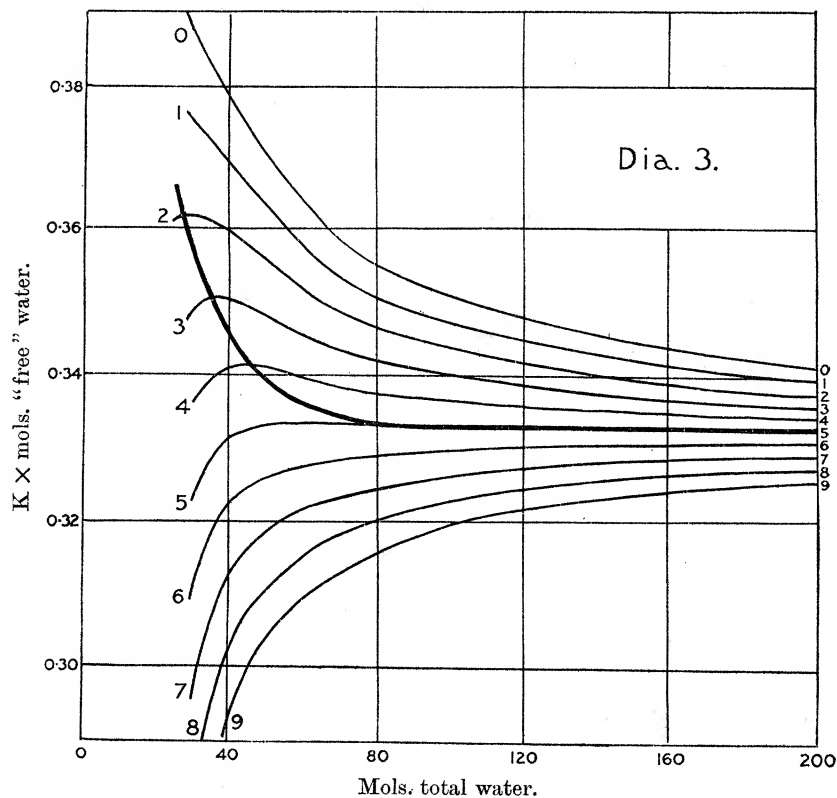
In the following sections "apparent hydration values" for the hydrogen chloride will be deduced from the velocities of hydrolysis and also from the equilibrium data. It must be pointed out, however, that although the proportion of water was always large, the values arrived at cannot be regarded as absolute, as they are dependent on the method of reckoning concentration. Moreover, this difficulty must always exist except in the case of extremely dilute solutions, as there is no method of expressing the concentrations and active masses of substances in concentrated solution that is free from defects.

The conditions obtaining in solutions are undoubtedly of so complex a character that the utmost care must be exercised not to put too rigid an interpretation on results arrived at on any one hypothesis.

F.—*Determination of Apparent Hydration Values of Hydrogen Chloride from the Relations between the Velocity Coefficients of Hydrolysis in the Case of Methylic Acetate and the Concentration of the Hydrogen Chloride.*

The apparent hydration values of hydrogen chloride at different concentrations have been determined from the data of the experiments described earlier on the assumption that part of the water is associated with or controlled by the acid and that the free water acts merely as solvent. The method used is the graphic one described in Part XII in connexion with the hydrolysis of cane sugar. Diagram 3 shows the process and the results obtained. Along the horizontal axis are given the total number of molecular proportions of water present to one of hydrogen chloride and on the vertical axis the products of the velocity coefficients and the molecular proportions of free water, *i.e.* water uncombined with the hydrogen chloride, on the various assumptions as to the number of molecular proportions of water attached to the acid. Each curve is based on the assumption that a number of molecular proportions of water equal to the number opposite the curve

have been removed from the sphere of solvent water. This number expresses accurately the water so removed at some definite concentration which has been taken as that corresponding to the maximum on the particular curve when the curve is at the point horizontal. It will be observed that the maxima on the different curves correspond to different concentrations. The



dark curve through the apices gives from the ordinates the specific molecular hydrolytic activity at different dilutions of the acid.

The apparent molecular hydration and molecular hydrolytic activity of the hydrogen chloride at different dilutions are given in the following table, in which are included for comparison the values deduced in the case of the hydrolysis of cane sugar (Part XII). (The hydrolytic activity values have been multiplied by 2.3026 to reduce them to the same unit as the methylic acetate values since in their calculation the velocity coefficient used was $K \times \log_{10} e$.)

Table V.

Molecular proportions of total water.	Apparent molecular hydration values.		Molecular hydrolytic activity.	
	(Methylic acetate.)	(Cane sugar.)	(Methylic acetate.)	(Cane sugar.)
30	2.5	12.4	356	518
40	3.5	13.6	345	486
50	4.2	15.1	339	465
60	4.6	16.8	336	444
70	4.9	18.2	334.5	
80	5.0	18.7	334	428
90	5.0	19.2	333.5	
100	5.0	19.8	333.5	419
200	5.0	—	333.5	

The data used in the calculations are given in Table III. A small error in any of the values of K makes a considerable irregularity in the curves. Thus, the values 354 and 443 produced irregularities, which were removed if the very slightly different values 351 and 444 were substituted; these values were consequently used instead of the mean values. Inspection of the list of values of K in Table III shows that probably they may be taken legitimately as the means. The regularity of the curves is a confirmation of the uniformity of the results.

It will be observed that the apparent molecular hydration values are much smaller than those deduced from the rate of inversion of cane sugar. This difference will be discussed in a later section (p. 601), after dealing with the apparent hydration values of salts. A constant value for the molecular hydration and the molecular hydrolytic activity is reached much earlier in the case of the hydrolysis of methylic acetate than in that of cane sugar. In this respect the results are very similar to those obtained from the hydrolysis of cane sugar by sulphuric acid and the monobasic sulphonic acids referred to in Part XXII.

G.—*Determination of Apparent Hydration Values from Equilibrium Data.*

In the section dealing with the change in the percentage of methylic acetate hydrolysed caused by changing the concentration of the hydrogen chloride (see p. 589), it was shown that increase in concentration of the acid catalyst was accompanied by an increase in the proportion of methylic acetate left unhydrolysed at equilibrium. If, therefore, the ratio of K' to K be calculated from the equilibrium data by means of the equation on p. 593, where

$$\frac{K'}{K} = \frac{[\text{CH}_3\text{COOCH}_3][\text{solvent water}][\text{catalyst}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{OH}][\text{catalyst}]},$$

this ratio must increase as the concentration of the hydrogen chloride is increased, provided that it be assumed that the amount of solvent water is not diminished by increase in the concentration of the hydrogen chloride, which could occur only if the acid were present in aqueous solution in an entirely unhydrated condition. As this is not the case, increase in the concentration of hydrogen chloride must undoubtedly be accompanied by an increase in the amount of water in combination with the acid and a corresponding decrease in the remaining solvent water. By decreasing the initial ratio of the water to the methylic acetate, a decrease in the percentage of the acetate hydrolysed, such as is observed in the experiments described above, is brought about. Three experiments were carried out in which the ratio of water to methylic acetate varied considerably. At the start there were approximately 5, 10, and 20 molecular proportions of acetate to 120 of water and 1 of hydrogen chloride. At equilibrium the percentages of methylic acetate hydrolysed were approximately 80, 68, and 55. It would appear, then, that although there may possibly be an actual increase in the ratio of K' to K (which would mean that the etherification was accelerated to a greater extent than the hydrolysis by an increase in the concentration of the catalyst, the increase is mainly and probably entirely apparent only and, if the correct value were taken for the solvent water, the ratio of K' to K would be constant.

Hydration values have been deduced on this last assumption from the equilibrium data on p. 590. It is to be noticed that the values obtained are not exactly comparable with those found in the previous section, in which the apparent hydration values are those of the hydrogen chloride in the presence of a great part of the unaltered methylic acetate. The values found from the equilibrium data are aggregate values for the various substances in solution at equilibrium, when relatively large amounts of acetic acid and methyl alcohol are present, both of which, no doubt, remove some water from the sphere of solvent.

In the following calculations, the degree of hydrolysis at equilibrium was taken not directly from the experimental values but from the curve (Diagram 2), which also gives the extrapolated value for the degree of hydrolysis that would be obtained in the absence of hydrogen chloride. From this latter value the true ratio of K' to K is obtained. At equilibrium 95 per cent. of the methylic acetate should be hydrolysed when no water is removed by hydrogen chloride. As there were originally 120 molecular proportions of water to 1 of methylic acetate, we have at equilibrium 119.05 of water, 0.05 of acetate and 0.95 of acetic acid and methylic alcohol. Hence

$$\frac{K'}{K} = \frac{0.05 \times 119.05}{0.95^2} = 6.6.$$

This value for the ratio of K' to K is used to calculate the values of the factor for the solvent water in the presence of the different amounts of hydrogen chloride. For example, when one molecular proportion of hydrogen chloride is used we have, since the percentage of methylic acetate hydrolysed is 94.6,

$$\frac{0.054 \times [\text{solvent water}]}{0.946^2} = 6.6 ;$$

whence the molecular proportions of solvent water are found to be 109.3. As 0.9 molecular proportions of water were used up for the hydrolysis, the apparent hydration value for the substances in solution at equilibrium (viz., one molecular proportion of hydrogen chloride and approximately one each of acetic acid and methylic alcohol) is equal to

$$120 - 0.9 - 109.3 = 9.8.$$

Table VI gives the apparent hydration values so obtained for the different concentrations of hydrogen chloride used.

Table VI.

A.	B.	C.	D.	E.	F.	G.
Molecules of HCl to 120 of H ₂ O.	Molecules of H ₂ O to 1 of HCl.	Fraction of acetate hydrolysed at equilibrium.	Molecules of solvent water. (H ₂ O).	Molecules combined water (H ₂ O).	Molecules combined H ₂ O per molecule HCl.	Molecules CH ₃ COOH and CH ₃ OH per molecule HCl.
0.0	—	0.95	119.05			
0.3	400	0.9487	115.7	3.4	11.3	3.3
0.6	200	0.9476	113.0	6.1	10.2	1.7
1.0	120	0.946	109.3	9.8	9.8	1.0
1.2	100	0.9452	107.5	11.6	9.7	0.8
1.5	80	0.944	105.0	14.1	9.4	0.6
2.0	60	0.942	100.9	18.2	9.1	0.5
3.0	40	0.9381	93.8	25.3	8.4	0.3
4.0	30	0.9341	87.3	31.8	8.0	0.25

Column A gives the molecular proportions of hydrogen chloride present to 120 of initial water.

Column B gives the molecular proportions of water (initial values) to one of hydrogen chloride.

Column C gives the molecular proportions of methylic acetate hydrolysed at equilibrium.

Column D gives the molecular proportions of solvent water calculated as above.

Column E gives the molecular proportions of water removed from the sphere of solvent, i.e. the apparent hydration values of the substances in solution.

Column F gives the apparent hydration values corresponding to one molecular proportion of hydrogen chloride and the other substances in solution (the approximate amounts of total water to one of hydrogen chloride being given in Column B).

Column G gives the approximate number of molecular proportions of acetic acid and methylic alcohol to one of hydrogen chloride.

To obtain the apparent hydration values of the hydrogen chloride, we should have to deduct from the numbers in Column F the unknown amount of water in combination with the number of molecules of acetic acid and methylic alcohol in Column G. This, however, would no doubt be small compared with that in combination with the hydrogen chloride.

It will be observed that the numbers are larger than those obtained in the previous section. The conditions are not the same, however. In this case the methylic acetate has been displaced (almost entirely) by methylic alcohol and acetic acid. The complexity of the conditions at equilibrium and the large effect produced by a very small experimental error prevent much weight being attached to the actual values obtained. They are of such an order, however, as to confirm the explanation advanced for the change in the degree of hydrolysis with change in the concentration of the catalyst.

H.—*Apparent Hydration Values of Salts.*

In view of the fact that lower values were obtained for the apparent hydration of hydrogen chloride from the rate of hydrolysis of methylic acetate than were obtained from the experiments on the rate of inversion of cane sugar, it appeared all the more desirable, as was stated in the introduction, to confirm the conclusions arrived at by Armstrong and Watson in Part IV that salts had a smaller concentrating effect in the former case than in the latter, *i.e.* that their apparent hydration values were smaller when methylic acetate was used as the hydrolyte than when cane sugar was used.

The apparent hydration values of the chlorides of sodium, potassium and ammonium were determined by a method similar to that described in Part XII in the case of the hydrolysis of cane sugar. In the experiments the molecular proportions used were 120 of water, 1 of methylic acetate, 2 of hydrogen chloride and 2 of salt. The values of the velocity coefficients were determined in the same way as for the acid alone. In the case of the ammonium chloride, phenolphthalein could not be used as an indicator and litmus was far from satisfactory. The results are consequently not very trustworthy. The results of the three experiments are given in the following table. The value of the constant obtained when the same proportion

of hydrogen chloride was used alone was 606. The apparent hydration values were obtained by taking the horizontal distances between the curve for the acid alone and those for the acid in the presence of the salts. Since the velocity of hydrolysis in the presence of the salts was determined for one concentration only, the hydration values could not be determined for different concentrations. The curves were assumed to be parallel to the acid curve at the point considered.* The apparent molecular hydration values obtained when 60 molecular proportions of total water were present for 1 of salt were approximately 3 for ammonium chloride and 5 each for sodium and potassium chlorides, that for sodium chloride being slightly the larger. The values obtained by Armstrong and Watson were considerably larger, being 5, 8 and 10 respectively in the presence of 55.5 molecular proportions of water. The general conclusion arrived at by Armstrong and Watson, however, is confirmed and the low values obtained for the salts are in complete harmony with the values obtained for the hydrogen chloride.

Table VII.

Percentage composition.	$K \times 10^5$.		
	NaCl.	KCl.	NH ₄ Cl.
20	—	662	
25	—	673	651
30	—	668	657
35	682	671	631
40	676	670	638
45	673	671	637
50	678	660	637
55	671	669	622
60	665	672	
65	666	661	
70	662		
Mean	672	668	639

I.—*Discussion of the Apparent Hydration Values arrived at in the Previous Sections.*

The method by which the apparent hydration value of the salts was deduced in the previous section is entirely distinct from that used to calculate the corresponding values for chlorhydric acid in Sections F and G. In the case of the salts no assumptions are necessarily made with regard to the actual cause of their observed accelerating effect on the rate of

* In Diagram 1 the values of the velocity coefficients for the hydrolysis in the presence of the three salts are indicated by crosses.

hydrolysis. The values are deduced directly from the values found experimentally for the rate of hydrolysis in the absence and presence of salts and merely express the accelerating effect of the salt in terms of the amount of water that would have to be removed from the system in order to produce the same effect on the rate of hydrolysis. Whilst it is believed that the accelerating effect of salts is mainly due to the concentrating effect they exercise, still the fact has never been lost sight of that their influence is of a much more complicated nature, the effect observed being the sum of various effects. In the case of the methods of deducing the apparent hydration values of the acid, however, the assumption was made that the acid removed water from the system—that it actually reduced the amount of solvent water. It has already been pointed out that it is not to be expected that the values arrived at in Section G would be the same as those arrived at in Section F but would be larger. The comparatively large effect that quite small differences in the experimental values used for the deduction of the apparent hydration values have on their magnitude prevents too great stress being laid on the actual values arrived at in Sections F and G; still, taking into account the differences in the conditions under which the apparent hydration values of the acids and of the salts were determined, the similarity of the order of magnitude of the values is of a most striking nature.

More interesting still is the comparison between the above results and those arrived at in the case of the hydrolysis of cane sugar. In this case, also, there was a singularly close relationship between the values arrived at for the acids and those for the salts. There is, however, a wide difference between the values arrived at both for acids and salts in the two cases, the use of cane sugar giving much higher values than when methylic acetate is employed. The cause of this difference is not easy to locate. It may be due to some extent to difference in the two methods of following the course of the interaction. The polarimetric method, whilst giving extremely uniform results, is full of complexities, some of which have already been dealt with in Part XII; others are discussed in Part XXII. It is not impossible that the method does not give a perfectly true record of the rate of change. On the other hand, there is much to show that there is an actual difference due to the character and influence of the hydrolytes. The effect of substances such as methylic acetate on other substances in solution is very different from the effect of cane sugar. The large effect that substances which have no great affinity for water, such, for instance, as propylic alcohol, with which methylic acetate may well be compared, have in reducing the solubility of salts in water would tend to show that such substances have a

large effect on the condition of other substances in solution. Cane sugar has an entirely different effect and it is highly probable that the actual condition of the salts and acids is different in the presence of even small amounts of methylic acetate from what it is in the presence of cane sugar.

With regard for the graphic method used to deduce the apparent hydration values of the acid, the results appear in every way to show that this form of treatment is valid in principle. The curves in the case of the hydrolysis of methylic acetate resemble in every way those obtained when cane sugar is used, the difference in the magnitude of the apparent hydration values arrived at being in accord with the difference in the corresponding values for the salts arrived at by an independent method.

Summary.

1. The rate of hydrolysis at 25° C. of methylic acetate in dilute aqueous solution under the catalytic influence of chlorhydric acid has been studied with a view to determine the apparent molecular hydration of the acid by the method used in connexion with the hydrolysis of cane sugar (Part XII) and further to ascertain whether the magnitude of the apparent hydration values of the acid and of salts be dependent on the nature of the hydrolyte. The molecular proportions of the substance used were 120 of water (H₂O), 1 of methylic acetate and from 0.6 to 4 of hydrogen chloride (Sections A and B).

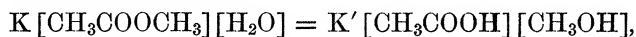
2. It is found that in no experiment did the degree of hydrolysis exceed 95 per cent. of the methylic acetate taken and that it is not justifiable either to adopt the usual assumption that in the presence of so large an excess of water the hydrolysis is practically complete or to treat the interaction as a case of simple unimolecular change. In the calculation of the velocity coefficients of hydrolysis, allowance has been made for the reverse change of etherification, the equation used being

$$dx/dt = K(a-x) - K'x^2,$$

in which a is the initial concentration of the methylic acetate and x the amount changed at time t . The rate of change dx/dt corresponding to different concentrations of unhydrolysed acetate was found directly from the experimental curve, the ratio of K' to K being found from the equilibrium data (Section C).

3. When the initial proportions of water and methylic acetate are the same, the amount of the latter hydrolysed at equilibrium depends on the concentration of the hydrogen chloride present, decreasing as the concentration of the catalyst increases (Section D).

4. In Section E it is shown that the equation always used to express the conditions at equilibrium, viz. :—



has in the past been much misunderstood and that, even though the relationship expressed hold good for different proportions of the various substances, the factor $[\text{H}_2\text{O}]$ does not necessarily stand for one of the substances entering directly into the interaction but probably expresses the degree of dilution. The view is advanced that hydrolysis is probably effected by the direct interaction of a unit of hydrated hydrolyte with one of the hydrated catalyst, the water uncombined with the acid catalyst functioning merely as solvent.

5. Apparent molecular hydration values of the catalyst (chlorhydric acid) have been deduced from the velocity coefficients of hydrolysis by the method developed in Part XII and also from the equilibrium data. Corresponding values for various salts have been found from the increase they produce in the velocity coefficient, on the assumption that the increase is due mainly to their concentrating effect. The values obtained both for the acid and for the salts are much lower than the corresponding values found when cane sugar and raffinose were used as hydrolytes. This difference may be due to some extent to the difference in the method used of following the course of the interaction but it is probable that there is a considerable actual difference in the condition of the acid and of the salts in the presence of such different hydrolytes as methylic acetate and cane sugar; furthermore that the hydrolytes are themselves different in character (Sections F–I).

The curves obtained in the deduction of the apparent hydration values of the acid are similar to those obtained in the case of cane sugar hydrolysis. The apparent hydration values increase with dilution to a maximum, whilst there is a corresponding decrease to a minimum in the molecular hydrolytic activity of the acid. The results appear to confirm in every way the validity of the method used.

With regard to the explanation of hydrolysis put forward in this communication and in Part XII, it should be said that it appears to be in complete agreement with all the experimental facts, many of which are not in harmony with the explanations that have been based on the ionic dissociation hypothesis. The theory of the hydrolytic process is discussed more at length in the following communication.